

## BEST AVAILABLE COPY

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-263488

(43)Date of publication of application : 07.10.1997

(51)Int.Cl.

C30B 29/04  
H01L 21/205  
H01L 21/208  
H01L 21/314

(21)Application number : 08-072732

(71)Applicant : MATSUSHITA ELECTRIC IND CO  
LTD

(22)Date of filing : 27.03.1996

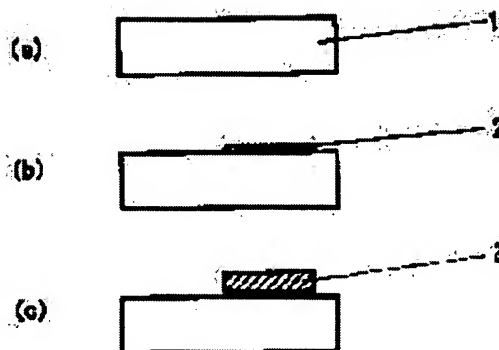
(72)Inventor : DEGUCHI MASAHIRO  
HIRAKI AKIO  
ITO TOSHIMICHI  
HATTA AKIMITSU  
MAKITA HIROSHI  
KITAHATA MAKOTO

## (54) PRODUCTION OF DIAMOND FILM

## (57)Abstract:

PROBLEM TO BE SOLVED: To efficiently generate nuclei at the time of synthesizing diamond by an easy means with satisfactory reproducibility and to form a high quality diamond film only in a desired region.

SOLUTION: A soln. contg. dispersed particles of  $\leq 0.1\mu\text{m}$  average particle diameter is applied to a region on a substrate 1 and a diamond film 3 is grown on the substrate 1. The uniformity and reproducibility of the grown diamond film 3 are considerably improved and a desired diamond film pattern can be formed while growing the diamond film.



## LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

\* NOTICES \*

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

CLAIMS

---

[Claim(s)]

[Claim 1] The manufacture approach of the diamond film which is the approach of forming the diamond film alternatively on a substrate material, and is characterized by including the process which applies the solution with which mean particle diameter made some fields on a substrate material distribute a particle 0.1 micrometers or less, and the process which grows up the diamond film on said substrate material.

[Claim 2] The manufacture approach of the diamond film characterized by to include the process at which mean particle diameter applies the solution which distributed the particle 0.1 micrometers or less on the substrate material which is the approach of forming the diamond film alternatively on a substrate material, and carried out the laminating of the sacrifice layer to some fields, the process which removes said sacrifice layer, and the process which grows up the diamond film on said substrate material.

[Claim 3] The manufacture approach of the diamond film which is the approach of forming the diamond film alternatively on a substrate material, and is characterized by including the process at which mean particle diameter applies the solution which distributed the particle 0.1 micrometers or less on a substrate material, the process which removes a part of field where said solution was applied, and the process which grows up the diamond film on said substrate material.

[Claim 4] The manufacture approach of the diamond film given in either of claims 1, 2, and 3 by which it is consisting [ the particle distributed in the solution which is the approach of forming alternatively and applies the diamond film on a substrate material / of a diamond ] characterized.

[Claim 5] The manufacture approach of the diamond film given in either of claims 1, 2, and 3 by which it is being [ it is the approach of forming the diamond film alternatively on a substrate material and / the amounts of the particle distributed in the solution to apply / 0.01g or more per 1l. of solutions, and 100g or less ] characterized.

[Claim 6] The manufacture approach of the diamond film given in either of claims 1, 2, and 3 by which it is or more 1x10<sup>16</sup> per 1l. of solutions, and being [ it is the approach of forming the diamond film alternatively on a substrate material and / the number of the particles distributed in the solution to apply / 1x10<sup>20</sup> ] or less characterized.

[Claim 7] The manufacture approach of the diamond film given in either of claims 1, 2, and 3 by which it is being [ it is the approach of forming the diamond film alternatively on a substrate material and / the solution to apply / water or alcohol ] characterized.

[Claim 8] The manufacture approach of the diamond film given in either of claims 1, 2, and 3 characterized by dropping said solution at the substrate material which is the approach of forming the diamond film alternatively on a substrate material, and the method of application of a solution rotated.

[Claim 9] The spreading consistency of the particle which is the approach of forming the diamond film alternatively on a substrate material, and was applied on the substrate material is per [ 1x10<sup>8</sup> ] square centimeter. The manufacture approach of the diamond film given in either of claims 1, 2, and 3 characterized by being more than an individual.

[Claim 10] The manufacture approach of the diamond film given in either of claims 1, 2, and 3 to which the substrate material which is the approach of forming alternatively and uses the diamond film on a

substrate material is characterized by being silicon.

[Claim 11] The manufacture approach of the diamond film given in either of claims 1, 2, and 3 characterized by being the approach of forming the diamond film alternatively on a substrate material, and the sacrifice layer which carried out the laminating on the substrate material being photoresist material.

[Claim 12] The manufacture approach of the diamond film given in either of claims 1, 2, and 3 by which it is forming [ are the approach of forming the diamond film alternatively, and / the diamond film / by the vapor phase synthetic method ]-on substrate material characterized.

---

[Translation done.]

\* NOTICES \*

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

DETAILED DESCRIPTION

---

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the selective growth approach of the diamond film used as the semi-conductor in electronic industry, or an insulator layer especially about the manufacture approach of the diamond film.

[0002]

[Description of the Prior Art] Also industrially, the diamond film formed by approaches, such as a chemistry vapor phase synthetic method (CVD method), attracts attention in recent years as the semi-conductor which has an unprecedented property, and an insulator layer ingredient. because, a diamond -- a wideband gap ingredient (forbidden-band width of face: about 5.5eV) -- it is -- the property -- doping - the possibility of semi-conductor-izing, a high degree of hardness, abrasion resistance, and high temperature conductivity -- it is inactive chemically -- etc. -- it is because it is very suitable as an electronic device ingredient of various fields. In addition, generally a diamond can form a carbon system type of gas and hydrogen gas with the vapor phase synthetic method made into material gas, and has a predominance also the manufacture-field.

[0003] However, in case the actually good diamond film is formed, control of the growth nucleus in the initial process of formation is important. It is because it is difficult for the growth origination of nucleus to make it the shape of film few when the diamond film is formed without generally processing in any way on substrate materials, such as silicon. so, " which installs a substrate material into the solution in which the diamond abrasive grain (particle size: several micrometers - dozens of micrometers) was made to mix, impresses a supersonic wave, and usually damages the front face of a substrate material as pretreatment of a substrate material as a conventional technique -- it damages and processing" is performed.

[0004] Moreover, there is patterning of the diamond film in one of the techniques for using the obtained diamond film industrially. As the patterning approach of the diamond film of having a desired configuration, only a desired field has etching which performs removal of the selection grown method into which the diamond film is grown up, or the garbage after film formation. As a conventional technique, the former forms the part which processes by the above damaging, and the part which is not performed on a substrate material, and the technique of growing up the film only into a desired field is performed. Moreover, as the latter, the mask material patternized on the diamond film is arranged, and the technique of removing only an unnecessary diamond layer by the dry etching using oxygen gas etc. is performed.

[0005]

[Problem(s) to be Solved by the Invention] Although it damaged conventionally and processing was made if the substrate material for urging the karyogenesis of a diamond as mentioned above was pretreated, there was a trouble that the homogeneity within a field of processing was inadequate, to a substrate material with a big area. Moreover, it obtained and damaged for every processing batch, and the technical problem occurred also in the point of the repeatability of effectiveness. Consequently, the

selective growth which it damages [ selective growth ] and grows up the diamond film only into a desired field in the processing section and the unsettled section had a technical problem in respect of repeatability etc. similarly.

[0006] Moreover, etching of the diamond film performed by forming mask material had technical problems, like there is possibility that the structure of a diamond film front face will change etc. by carrying out the laminating of that a diamond is comparatively hard to be etched or the mask material while the process which forms mask material, and the process to remove were given.

[0007] therefore , this invention aim at offer the approach of the selective growth which form a good diamond film only in a desired field while it perform karyogenesis at the time of diamond composition often [ repeatability ] and efficiently by simple technique by mean particle diameter apply to some substrate materials the solution which distributed the particle 0.1 micrometers or less , and grow up a diamond film on said substrate material further in order to solve said technical problem in the conventional technique .

[0008]

[Means for Solving the Problem] The selective-growth approach of the diamond film applied to this invention in order to attain said purpose is the approach of forming the diamond film alternatively on a substrate material, and is the selective-growth approach of the diamond film characterized by to include the process which applies the solution with which mean particle diameter made some fields on a substrate material distribute a particle 0.1 micrometers or less, and the process which grows up the diamond film on said substrate material.

[0009] In order to attain said purpose, moreover, the selective growth approach of the diamond film concerning this invention The process at which mean particle diameter applies the solution which distributed the particle 0.1 micrometers or less on the substrate material which is the approach of forming the diamond film alternatively on a substrate material, and carried out the laminating of the sacrifice layer to some fields, It is the selective growth approach of the diamond film characterized by including the process which removes said sacrifice layer, and the process which grows up the diamond film on said substrate material.

[0010] In order to attain said purpose, moreover, the selective growth approach of the diamond film concerning this invention The process at which it is the approach of forming the diamond film alternatively on a substrate material, and mean particle diameter applies the solution which distributed the particle 0.1 micrometers or less on a substrate material, It is the selective growth approach of the diamond film characterized by including the process which removes a part of field where said solution was applied, and the process which grows up the diamond film on said substrate material.

[0011] Moreover, as for this invention, in said selective growth approach, it is desirable that the particle distributed in the solution to apply consists of a diamond.

[0012] Moreover, as for this invention, in said selective growth approach, it is desirable that the amounts of the particle distributed in the solution to apply are 0.01g or more per 1l. of solutions and 100g or less. The amounts of a particle are 0.1g or more per 1l. of solutions, and 20g or less still more preferably.

[0013] Moreover, as for this invention, in said selective growth approach, it is desirable  $1 \times 10^{16}$  or more per 1l. of solutions and that the number of the particles distributed in the solution to apply is [ or less ]  $1 \times 10^{20}$ . The number of particles is [  $1 \times 10^{17}$  or more per 1l. of solutions, and / or less ]  $1 \times 10^{19}$  still more preferably.

[0014] Moreover, as for this invention, in said selective growth approach, it is desirable that the solution to apply is water or alcohol.

[0015] Moreover, as for this invention, in said selective growth approach, it is desirable that said solution is dropped at the substrate material which the method of application of a solution rotated.

[0016] Moreover, for this invention, the spreading consistency of the particle applied on the substrate material in said selective growth approach is per [  $1 \times 10^8$  ] square centimeter. It is desirable that it is more than an individual. A spreading consistency is per [  $1 \times 10^9$  ] square centimeter still more preferably. It is more than an individual.

[0017] Moreover, as for this invention, in said selective growth approach, it is desirable that the

substrate material to be used is silicon.

[0018] Moreover, as for this invention, in said selective growth approach, it is desirable that the sacrifice layer which carried out the laminating on the substrate material is photoresist material.

[0019] Moreover, as for this invention, in said selective growth approach, it is desirable that the diamond film is formed by the vapor phase synthetic method.

[0020] according to the configuration of this invention approach, it be the approach of form the diamond film alternatively on a substrate material, and since it be characterize by include the process which apply the solution with which mean particle diameter made some fields on a substrate material distribute a particle 0.1 micrometers or less, and the process which grow up the diamond film on said substrate material, the following operations can be do so.

[0021] As for a particle 0.1 micrometers or less, the mean particle diameter applied on the substrate material serves as a site of a growth nucleus in the initial process of diamond film formation. So, control of the growth nucleus at the time of diamond film formation is attained by controlling the number and spreading location of a particle to apply artificially. While the former damages the number of particles and the control of a location which are applied, they are simple as compared with processing and the homogeneity and repeatability of the growth film improve markedly as a result in that case, it becomes possible to obtain a desired diamond film pattern to diamond film growth and coincidence. Although effectiveness is enough acquired as mean particle diameter of the particle to be used by being referred to as 0.1 micrometers or less as above-mentioned, the smaller possible one is good and mean particle diameter is 0.05 micrometers or less desirably.

[0022] Moreover, the process at which mean particle diameter applies the solution which distributed the particle 0.1 micrometers or less on the substrate material which according to the configuration of said this invention approach is the approach of forming the diamond film alternatively on a substrate material, and carried out the laminating of the sacrifice layer to some fields, Since it is characterized by including the process which removes said sacrifice layer, and the process which grows up the diamond film on said substrate material, the following operations can be done so.

[0023] That is, although growth of the diamond film is easily attained because mean particle diameter applies a particle 0.1 micrometers or less on a substrate material as mentioned above, while separation of the growth field of the diamond film becomes easy by using a sacrifice layer as an approach of separating a spreading field, detailed pattern formation becomes easy.

[0024] Moreover, the process at which according to the configuration of said this invention approach it is the approach of forming the diamond film alternatively on a substrate material, and mean particle diameter applies the solution which distributed the particle 0.1 micrometers or less on a substrate material, Since it is characterized by including the process which removes a part of field where said solution was applied, and the process which grows up the diamond film on said substrate material, while separation of the growth field of the diamond film becomes easy like the above-mentioned configuration, detailed pattern formation becomes easy.

[0025] Moreover, in the configuration of this invention approach, since the particle used as a growth nucleus is a diamond particle according to the desirable example that the particle distributed in the solution to apply consists of a diamond, it becomes possible to obtain the good diamond film.

[0026] The amount of the particle distributed in the configuration of this invention approach in the solution to apply Moreover, 0.01g or more per 1l. of solutions, According to the desirable example that they are 0.1g or more per 1l. of solutions, and 20g or less still more desirably, 100g or less of diamonds which grow considering a spreading particle as a nucleus becomes possible [ applying easily the particle number of amount sufficient in a short time to become film-like on a substrate material ]. When particle size is about 1g and particle size is 0.04 micrometers in general 0.01-micrometer case as optimal particle weight in that case also depending on the particle size of the particle to be used, it is about 16g in general.

[0027] The number of the particles distributed in the configuration of this invention approach in the solution to apply Moreover,  $1 \times 10^{16}$  or more per 1l. of solutions According to the desirable example that they are  $1 \times 10^{17}$  or more per 1l. of solutions, and  $1 \times 10^{19}$  pieces or less still more desirably,  $1 \times 10^{20}$  or

less pieces The diamond which grows considering a spreading particle as a nucleus becomes possible [ applying easily the particle number of amount sufficient in a short time to become film-like on a substrate material ] like the above-mentioned configuration.

[0028] Moreover, in the configuration of this invention approach, according to the desirable example that the solution to apply is water or alcohol, while the treatment of a solution is easy, it is the optimal as a distributed solvent of a particle.

[0029] Moreover, according to the desirable example that said solution is dropped at the substrate material which the method of application of a solution rotated, in the configuration of this invention approach, it becomes possible to apply a solution with uniformly and sufficient repeatability also to the substrate material of a big area.

[0030] Moreover, the spreading consistency of the particle applied on the substrate material in the configuration of this invention approach is per [  $1 \times 10^8$  ] square centimeter. It is per [  $1 \times 10^9$  ] centimeter still more desirably more than an individual. According to the desirable example that it is more than an individual, since the karyogenesis consistency of a big diamond can be obtained in the early stages of growth, a film-like diamond can be obtained in a short time.

[0031] Moreover, in the configuration of this invention approach, according to the desirable example that the substrate material to be used is silicon, while a process configuration becomes easy, fusion in the component and diamond layer using silicon is attained.

[0032] Moreover, in the configuration of this invention approach, while patterning is possible using the photolithography process usually used according to the desirable example that the sacrifice layer which carried out the laminating on the substrate material is photoresist material, it becomes a simple process configuration.

[0033] Moreover, according to the desirable example that the diamond film is formed by the vapor phase synthetic method, in this invention configuration, the good diamond film can be formed easily.

[0034]

[Embodiment of the Invention] Hereafter, this invention is explained still more concretely using an example.

[0035] <Gestalt of the 1st operation> drawing 1 is the schematic diagram of one example of the selective growth approach concerning this invention approach.

[0036] A substrate material is prepared first. ( Drawing 1 (a)) Although especially the ingredient used as this base material material is not limited, silicon is used well. The 2 inches silicon substrate 1 was used also in this example.

[0037] Then, after defecating this silicon substrate 1 at the usual washing process, mean particle diameter applied to some fields on a silicon substrate 1 the solution which distributed the diamond particle 2 which is 0.01 micrometers. ( Drawing 1 (b)) In this example, the 2g diamond particle 2 was distributed to 1l. pure water, and the solution which added 2 morel. ethanol was used. That is, about 0.67g per 1l. of solutions and the solution with which about  $4 \times 10^{17}$  diamond particles 2 per 1l. of solutions were contained as a particle number were used as particle weight. Spreading of a solution was performed by dropping a solution directly on a silicon substrate 1. The silicon substrate 1 was dried by the exposure of infrared lamp light after spreading.

[0038] The diamond film 3 was formed with the vapor phase synthetic method on the silicon substrate 1 to which the diamond particle 2 was furthermore applied. ( Drawing 1 (c)) Although especially limitation is not carried out as the synthetic approach of the diamond film, it is well used from a vapor phase synthetic method being easy. Generally the gaseous-phase composition approach is performed by decomposing the material gas into material gas using what diluted the carbon source of organic compounds, such as hydrocarbon gas, such as methane, ethane, ethylene, and acetylene, alcohol, and an acetone, a carbon monoxide, etc. with hydrogen. Oxygen, water, etc. can also be further added suitably to material gas in that case. Although especially limitation was not carried out about the applicable vapor phase synthetic method, in this example, the diamond film was formed by the microwave plasma-CVD method. A microwave plasma-CVD method is the approach of plasma-izing and forming a diamond by impressing microwave to material gas. As concrete conditions, the carbon monoxide gas



diluted with hydrogen by about 1-10vol% was used for material gas. Reaction temperature and a pressure are 800-900 degrees C and 25 - 40Torr, respectively.

[0039] As a result of forming the diamond film on a silicon substrate by the above approaches, it was checked that the diamond film has grown to be only the part which applied the solution. Moreover, as compared with the case where the former also damaged the film production time amount which the grown-up diamond consists film-like of, and it forms a diamond by processing, it turned out that one half extent is shortened. This is considered to originate in the karyogenesis consistency of a diamond being very large. Then, as a result of investigating the karyogenesis consistency in the growth early stages of the diamond in this example, it was checked that it is larger than about  $1 \times 10^{11}$  per square centimeter and the conventional substrate pretreatment approach about single figure. That is, it was checked that the selective growth of the good diamond film can be carried out more efficiently than before.

[0040] Moreover, the same result was obtained when the particle size and the amount of a diamond particle which are applied when the diamond film is grown up on other formation conditions were changed, a solution was prepared, and a particle was further changed into silicon carbide.

[0041] <Gestalt of the 2nd operation> drawing 2 is the schematic diagram of other one example of the selection grown method concerning this invention approach.

[0042] A substrate material is prepared first. (Drawing 2 (a)) Although especially the substrate material ingredient was not limited in this configuration, the 2 inches silicon substrate 4 was used in this example.

[0043] Next, after defecating this silicon substrate 4 at the usual washing process, the photoresist material 5 with a thickness of about 2 micrometers was applied. (Drawing 2 (b)) Although not limited about the method of application, in this example, the photoresist material 5 was dropped at the rotated silicon substrate 4, and the approach of using as a coat and the so-called spin coat were used.

[0044] Then, patterning of the photoresist material 5 applied using the technique of the usual photolithography was performed. (Drawing 2 (c)) Although formed in the photoresist material 5 to which the aperture of a dot which consists a round dot with a diameter of 5 micrometers of  $100 \times 100$  pieces, i.e., 10000 pieces, at intervals of 20 micrometers in this example was applied, it can be made the configuration pattern of arbitration.

[0045] And on the silicon substrate 4 to which the laminating of the photoresist material 5 by which patterning was carried out was carried out, mean particle diameter applied the solution which distributed the diamond particle 6 which is 0.01 micrometers. (Drawing 2 (d)) The used solution is the same as that of the 1st example. Spreading of a solution used the technique of the spin coat same with having applied the photoresist material 5. The silicon substrate 4 was dried by the exposure of infrared lamp light after spreading.

[0046] Then, the solvent for resist removal was permeated 10 minutes or more in the silicon substrate 4 to which the diamond particle 6 was applied, and the photoresist material 5 was removed. (Drawing 2 (e)) Although it is dependent on the quality of the material of the photoresist to be used etc. as a solvent for resist removal, generally organic solvents, such as an acetone, can be used.

[0047] The diamond film 7 was formed by the microwave plasma-CVD method on the silicon substrate 4 from which the photoresist material 5 was furthermore removed. (Drawing 2 (f)) The synthetic conditions of the diamond film are the same as the 1st example.

[0048] As a result of forming the diamond film on a silicon substrate by the above approaches, it was checked that the diamond film has grown to be only the dot field it is 5 micrometers, whose part, i.e., diameter, which applied the solution. Moreover, when removing photoresist material, in spite of having permeated the solvent for resist removal, the pattern configuration of the formed diamond film was the same as that of the pattern of the field where the diamond particle was applied before photoresist removal, and the growth rate of a diamond of it was the same as that of the 1st example. This shows that it has adhered to stability on a substrate material by force, such as Van der Waals force, if an end diamond particle is applied on a substrate material.

[0049] In this example, although the photoresist was used as mask material which classifies the

spreading field of a particle, also when other ingredients were sufficient, for example, patterning was carried out after depositing the amorphous silicon film on a substrate material, and it considered as mask material, the same result was obtained.

[0050] Moreover, the same result was obtained when the particle size and the amount of a diamond particle which are applied when the diamond film is grown up on other formation conditions were changed, a solution was prepared, and a particle was further changed into silicon carbide.

[0051] <the gestalt of the 3rd operation> -- the above-mentioned example usually showed -- like -- the existence of particle spreading -- although selective growth was carried out enough, selective growth of the diamond film was performed on the surface, using as a substrate the silicon which has a diacid-ized silicon layer in order to raise selection growth possibility more. It is because a diamond generally hardly grows on diacid-ized silicon compared with a silicon top by gaseous-phase composition of a diamond. The schematic diagram of other one example of the selective growth approach which starts this invention approach at drawing 3 is shown.

[0052] A silicon substrate 8 is prepared first. ( Drawing 3 (a)) The 2 inches silicon substrate was used also in this example.

[0053] Then, after defecating this silicon substrate 8 at the usual washing process, the silicon substrate 8 was installed in the cylinder container made from a quartz, and thermal oxidation heated in a wet oxygen ambient atmosphere was performed. Thermal oxidation conditions are 1000 degrees C and 2 hours. Consequently, the diacid-ized silicon layer 9 was formed in the field of about 1 micrometer of surfaces of a silicon substrate 8 ( drawing 3 (b)).

[0054] Next, after applying the photoresist material 10 with a thickness of about 2 micrometers on a spin coat, the desired pattern was formed in the photoresist material 10 at the process of the usual photolithography. ( Drawing 3 (c)) The formation pattern is the same as that of the 2nd example.

[0055] Furthermore, etching removal of the diacid-ized silicon layer 9 of a silicon substrate surface was carried out by using the photoresist material 10 as a mask. ( Drawing 3 (d)) The wet etching which used the etching reagent of a FUTSU nitric-acid system performed etching of the diacid-ized silicon layer 9. Consequently, the aperture of the round dot whose diameter is 5 micrometers was formed in the part from which the diacid-ized silicon layer 9 was removed like the 2nd example.

[0056] And on the silicon substrate 8 to which the laminating of the photoresist material 10 and the diacid-ized silicon layer 9 by which patterning was carried out was carried out, mean particle diameter applied the solution which distributed the diamond particle 11 which is 0.01 micrometers. ( Drawing 3 (e)) The used solution is the same as that of the 1st example. Spreading of a solution used the technique of the spin coat same with having applied photoresist material. The silicon substrate 8 was dried by the exposure of infrared lamp light after spreading.

[0057] Then, the solvent for resist removal was permeated 10 minutes or more in the silicon substrate 8 to which the diamond particle 11 was applied, and the photoresist material 10 was removed. ( Drawing 3 (f)) The diamond film 12 was formed by the microwave plasma-CVD method on the silicon substrate 8 from which the photoresist material 10 was removed further. ( Drawing 2 (g)) The synthetic conditions of the diamond film are the same as the 1st example.

[0058] As a result of forming the diamond film on a silicon substrate by the above approaches, it was checked that the diamond film has grown to be only the dot field it is 5 micrometers, whose part, i.e., diameter, which applied the solution. And as a result of comparing with the 2nd example, improvement in the selection growth possibility was checked.

[0059] In this example, although the diacid-ized silicon layer was used as the quality of the material of the field where a diamond does not grow, other ingredients are sufficient, for example, the same result was obtained also in the silicon nitride layer.

[0060] Moreover, the same result was obtained when the particle size and the amount of a diamond particle which are applied when the diamond film is grown up on other formation conditions were changed, a solution was prepared, and a particle was further changed into silicon carbide.

[0061] <Gestalt of the 4th operation> drawing 4 is the schematic diagram of other one example of the selective growth approach concerning this invention approach.

[0062] A substrate material is prepared first. ( Drawing 4 (a)) Although especially limitation was not carried out for the substrate material ingredient in this configuration, the 2 inches silicon substrate 13 was used in the \*\*\*\* example.

[0063] Next, after defecating a silicon substrate 13 at the usual washing process, mean particle diameter applied the solution which distributed the diamond particle 14 which is 0.01 micrometers on the silicon substrate 13. ( Drawing 4 (b)) The used solution is the same as that of the 1st example. Spreading of a solution used the technique of the same spin coat as the 2nd example. The silicon substrate 13 was dried by the exposure of infrared lamp light after spreading.

[0064] Then, the photoresist material 15 with a thickness of about 2 micrometers was applied on the spin coat ( drawing 4 (c)).

[0065] And patterning of the photoresist material 15 applied by the technique of the usual photolithography was performed. ( Drawing 4 (d)) It formed by the photoresist material 10 to which the dot which consists a round dot with a diameter of 5 micrometers of 100x100 pieces, i.e., 10000 pieces, at intervals of 20 micrometers in this example was applied, and other parts were removed.

[0066] A part of silicon substrate 13 was etched by using as a mask the photoresist material 15 by which patterning was furthermore carried out. ( Drawing 4 (e)) About the approach of etching, although especially limitation was not carried out, it carried out etching removal only of about 2 micrometers of the silicon substrates of a non-mask field by this example by reactive ion etching (RIE) using the chlorofluorocarbon which mixed oxygen.

[0067] Then, the solvent for resist removal removed the photoresist material 15 ( drawing 4 (f)).

[0068] The diamond film 16 was formed in silicon substrate top 13 from which the photoresist material 15 was furthermore removed by the microwave plasma-CVD method. ( Drawing 4 (g)) The synthetic conditions of the diamond film are the same as the 1st example.

[0069] As a result of forming the diamond film on a silicon substrate by the above approaches, it was checked that the diamond film has grown to be only the dot field it is 5 micrometers, whose part, i.e., diameter, which applied the solution. Moreover, when removing photoresist material, in spite of having permeated the solvent for resist removal, it was checked that the pattern configuration of the formed diamond film is the same as that of the pattern of the field where the diamond particle was applied before photoresist removal, and the growth rate of a diamond is the same as that of the 1st example.

[0070] In this example, although reactive ion etching was used as etching of a substrate material performed in order to classify the spreading field of a particle, other technique is sufficient, for example, the result with the same said of the wet etching using the solution of a FUTSU nitric-acid system was obtained.

[0071] Moreover, the same result was obtained when the particle size and the amount of a diamond particle which are applied when the diamond film is grown up on other formation conditions were changed, a solution was prepared, and a particle was further changed into silicon carbide.

[0072] For the comparison with the example indicated to the <example of comparison> above, into the solution, the bigger diamond particle than 0.1 micrometers was mixed, and the same experiment was conducted. Consequently, the karyogenesis consistency in the initial process of diamond growth was low single or more figures as compared with the above-mentioned example, and needed twice [ more than ] as many film production time amount as this to become film-like as a result. Moreover, nonuniformity was in the thickness distribution in a substrate front face, and it was lacking in homogeneity. Furthermore, it was checked that the selection growth possibility of the particle spreading section and an uncoated portion also falls remarkably.

[0073]

[Effect of the Invention] As mentioned above, according to the configuration of the selective growth approach concerning this invention approach, it is the approach of forming the diamond film alternatively on a substrate material. Since it is characterized by including the process at which mean particle diameter applies to some fields on a substrate material the solution which distributed the particle 0.1 micrometers or less, and the process which grows up the diamond film on said substrate material, While the homogeneity and repeatability of the diamond film which grow improve markedly, it becomes

possible to obtain a desired diamond film pattern to diamond film growth and coincidence.

[0074] Moreover, according to the configuration of the selective growth approach concerning this invention approach, it is the approach of forming the diamond film alternatively on a substrate material. The process at which mean particle diameter applies the solution which distributed the particle 0.1 micrometers or less on the substrate material which carried out the laminating of the sacrifice layer to some fields, Since it is characterized by including the process which removes said sacrifice layer, and the process which grows up the diamond film on said substrate material and separation of the growth field of the diamond film becomes easy while the diamond film grows efficiently, detailed pattern formation becomes easy.

[0075] Moreover, the process at which according to the configuration of the selective growth approach concerning this invention approach it is the approach of forming the diamond film alternatively on a substrate material, and mean particle diameter applies the solution which distributed the particle 0.1 micrometers or less on a substrate material, Since it is characterized by including the process which removes a part of field where said solution was applied, and the process which grows up the diamond film on said substrate material and separation of the growth field of the diamond film becomes easy like the above-mentioned configuration, detailed pattern formation becomes easy.

[0076] By using as a diamond the particle distributed in the solution furthermore applied, it becomes possible to obtain the good diamond film.

[0077] It becomes possible to apply easily the particle number of amount sufficient in a short time for a diamond to become film-like on a substrate material by setting still more desirably to 0.1g or more per 1l. of solutions, and 20g or less 0.01g or more per 1l. of solutions of 100g or less of amounts of the particle distributed in the solution furthermore applied.

[0078] A diamond becomes possible [ applying easily the particle number of sufficient amount to become film-like on a substrate material ] like the above-mentioned configuration for a short time by making still more desirably into  $1 \times 10^{17}$  or more per 1l. of solutions, and  $1 \times 10^{19}$  pieces or less the  $1 \times 10^{16}$  or more number [  $1 \times 10^{20}$  or less ] per 1l. of solutions of the particles distributed in the solution furthermore applied.

[0079] By using as water or alcohol the solution furthermore applied, the treatment of a solution becomes easy.

[0080] By considering as solution dropping for the substrate material which furthermore rotated the method of application of a solution, it becomes possible to apply a solution with uniformly and sufficient repeatability also to the substrate material of a big area.

[0081] It is the spreading consistency of the particle furthermore applied on the substrate material per [  $1 \times 10^8$  ] square centimeter. It is per [  $1 \times 10^9$  ] centimeter still more desirably more than an individual. A film-like diamond can be obtained by carrying out to more than an individual in a short time.

[0082] While a process configuration becomes easy by using as silicon the substrate material furthermore used, fusion in the component and diamond layer using silicon is attained.

[0083] Since patterning is possible using the photolithography process usually used by making into photoresist material the sacrifice layer which furthermore carried out the laminating on the substrate material, it becomes a simple process configuration.

[0084] By furthermore forming the diamond film with a vapor phase synthetic method, the good diamond film can be formed easily.

---

[Translation done.]



(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開

特開平9-

(43) 公開日 平成9年(

(51) Int.Cl. <sup>6</sup>	識別記号	片内整理番号	P I	
C 3 0 B	29/04		C 3 0 B	29/04 Q
H 0 1 L	21/205		H 0 1 L	21/205
	21/208			21/208 Z
	21/314			21/314 A
審査請求 未請求 請求項の数12 O L				
(21) 出願番号	特願平8-72732		(71) 出願人	000005821
(22) 出願日	平成8年(1996)3月27日			松下電器産業株式会社
				大阪府門真市大字門真1006番
			(72) 発明者	出口 正洋
				大阪府門真市大字門真1006番
				産業株式会社内
			(72) 発明者	平木 昭夫
				滋賀県草津市南笠町91 南笠
			(72) 発明者	伊藤 利道
				大阪府箕面市小野原東6-28
			(72) 発明者	八田 章光
				大阪府吹田市片山町2-2-1
			(74) 代理人	弁理士 滝本 智之 (外1)

(54) 【発明の名称】 ダイヤモンド膜の製造方法

(57) 【要約】

【課題】 ダイヤモンド合成時の核発生を簡便な手法で再現性良くかつ効率的に行なうと共に、所望の領域にのみ良質なダイヤモンド膜を形成する方法を提供する。

【解決手段】 基板素材上の一部の領域に平均粒径が0.1 μm以下の粒子を分散させた溶液を塗布する。基板素材上にダイヤモンド膜を成長させる。これにより、成長するダイヤモンド膜の均一性や再現性が格段向上すると共に、ダイヤモンド膜成長と同時に、所望のダイヤモンド膜パターンを得ることが可能となる。

(a)



(b)



1

【特許請求の範囲】

【請求項１】 基板素材上にダイヤモンド膜を過剰的に形成する方法であって、基板素材上の一部の領域に平均粒径が $0.1\mu\text{m}$ 以下の粒子を分散させた溶液を塗布する工程と、前記基板素材上にダイヤモンド膜を成長させる工程とを含むことを特徴とするダイヤモンド膜の製造方法。

【請求項2】 基板素材上にダイヤモンド膜を選択的に形成する方法であって、一部の領域に犠牲層を積層した基板素材上に平均粒径が $0.1\mu\text{m}$ 以下の粒子を分散させた溶液を塗布する工程と、前記犠牲層を除去する工程と、前記基板素材上にダイヤモンド膜を成長させる工程とを含むことを特徴とするダイヤモンド膜の製造方法。

【請求項3】 基板素材上にダイヤモンド膜を選択的に形成する方法であって、基板素材上に平均粒径が0.1 μm以下の粒子を分散させた溶液を塗布する工程と、前記溶液が塗布された領域の一部を除去する工程と、前記基板素材上にダイヤモンド膜を成長させる工程とを含むことを特徴とするダイヤモンド膜の製造方法。

【請求項4】 基板素材上にダイヤモンド膜を選択的に形成する方法であって、塗布する溶液中に分散させた粒子が、ダイヤモンドからなること特徴とする請求項1、2、3のいずれかに記載のダイヤモンド膜の製造方法。

【請求項5】 基板素材上にダイヤモンド膜を選択的に形成する方法であって、塗布する溶液中に分散させた粒子の量が、溶液1リットル当たり0.01g以上、100g以下であること特徴とする請求項1、2、3のいずれかに記載のダイヤモンド膜の製造方法。

【請求項6】 基板素材上にダイヤモンド膜を選択的に形成する方法であって、塗布する溶液中に分散させた粒子の数が、溶液1リットル当たり $1 \times 10^9$ 個以上、 $1 \times 10^9$ 個以下であること特徴とする請求項1、2、3のいずれかに記載のダイヤモンド膜の製造方法。

【請求項7】 基板素材上にダイヤモンド膜を選択的に形成する方法であって、塗布する溶液が、水あるいはアルコールであること特徴とする請求項1、2、3のいずれかに記載のダイヤモンド膜の製造方法。

【請求項 8】 基板素材上にダイヤモンド膜を選択的に形成する方法であって、溶液の塗布方法が、回転した基板素材に前記溶液を滴下することを特徴とする請求項

2

記載のダイヤモンド膜の製造方法。

【請求項 11】 基板素材上にダイヤモンドに形成する方法であって、基板素材上に形成されるダイヤモンドが、フォトレジスト材であることを特徴する請求項 1、2、3 のいずれかに記載のダイヤモンド形成法。

【請求項１２】 基板素材上にダイヤモンドに形成する方法であって、ダイヤモンドの法によって形成されること特徴とする請求のいずれかに記載のダイヤモンド膜の製

【発明の詳細な説明】

[ 0001 ]

【発明の属する技術分野】本発明は、ダイヤモンド製造方法に関するもので、特に、電子工率体や絶縁体層として用いられるダイヤモンド成長方法に関する。

【0002】

【従来の技術】近年化学気相合成法（CVD法）によって形成されるダイヤモンド膜ない特性を有する半導体、絶縁体層材料も注目されている。なぜならダイヤモンドギャップ材料（禁制帯幅：約5.5eV）その特性はドーピングによって半導体化し、高硬度、耐磨耗性、高熱伝導率、化学的に不活性な様々な分野の電子素子材料として非常に有用である。加えてダイヤモンドは、一般に水素ガスを原料ガスとした気相合成法で製造可能であり、製造的な面でも優位性を持

【0003】しかしながら実際に良質な  
を形成する際には、形成初期過程にお  
が重要である。なぜなら一般的にシリ  
材上に何等処理することなくダイヤモンド  
場合、成長核の発生が少なく膜状にする  
らである。それ故に従来技術としては、  
前処理として、ダイヤモンド砥粒（粒径  
10 $\mu$ m）を混入させた溶液中に基板素材を  
を印加して基板素材の表面を傷付ける”  
行なっている。

【0004】また得られたダイヤモンド  
用するための技術の1つには、ダイヤモ

(3)

特開平 9 -

3

4

【0005】

【発明が解決しようとする課題】上記のようにダイヤモンドの核発生を促すための基板素材の前処理をしては、従来傷付け処理がなされているが、大きな面積を持つ基板素材に対して、処理の面内均一性が不十分であるという問題点があった。また処理バッチ毎に得られる傷付け効果の再現性の点においても課題があった。その結果、傷付け処理部と未処理部で所望の領域にのみダイヤモンド膜を成長させる選択成長も、同様に再現性などの点で課題があった。

【0006】またマスク材を形成して行なうダイヤモンド膜のエッチングは、マスク材を形成する工程や除去する工程が付与されると共に、ダイヤモンドが比較的エッチングされにくいことやマスク材を積層することによってダイヤモンド膜表面の構造が変化してしまう可能性などがあるなどの課題があった。

【0007】従って本発明は、従来技術における前記課題を解決するため、基板素材の一部分にのみ平均粒径が $0.1\mu\text{m}$ 以下の粒子を分散させた溶液を塗布し、さらに前記基板素材上にダイヤモンド膜を成長させることにより、ダイヤモンド台成時の核発生を簡便な手法で再現性良くかつ効率的に行なうと共に、所望の領域にのみ良質なダイヤモンド膜を形成する選択成長の方法を提供することを目的とする。

【0008】

【課題を解決するための手段】前記目的を達成するため、本発明に係るダイヤモンド膜の選択成長方法は、基板素材上にダイヤモンド膜を選択的に形成する方法であって、基板素材上の一部の領域に平均粒径が $0.1\mu\text{m}$ 以下の粒子を分散させた溶液を塗布する工程と、前記基板素材上にダイヤモンド膜を成長させる工程とを含むことを特徴とするダイヤモンド膜の選択成長方法である。

【0009】また前記目的を達成するため、本発明に係るダイヤモンド膜の選択成長方法は、基板素材上にダイヤモンド膜を選択的に形成する方法であって、一部の領域に犠牲層を積層した基板素材上に平均粒径が $0.1\mu\text{m}$ 以下の粒子を分散させた溶液を塗布する工程と、前記犠牲層を除去する工程と、前記基板素材上にダイヤモンド膜を成長させる工程とを含むことを特徴とするダイヤモンド膜の選択成長方法である。

らなることが好ましい。

【0012】また本発明は、前記選択成長で、塗布する溶液中に分散させた粒子の：トル当たり $0.01\text{g}$ 以上、 $100\text{g}$ 以下が好ましい。さらに好ましくは、粒子の重：トル当たり $0.1\text{g}$ 以上、 $20\text{g}$ 以下である。

【0013】また本発明は、前記選択成長で、塗布する溶液中に分散させた粒子の：トル当たり $1\times 10^9$ 個以上、 $1\times 10^{10}$ 個以下が好ましい。さらに好ましくは、粒子の：トル当たり $1\times 10^9$ 個以上、 $1\times 10^{10}$ 個以下である。

【0014】また本発明は、前記選択成長で、塗布する溶液が水あるいはアルコールが好ましい。

【0015】また本発明は、前記選択成長で、溶液の塗布方法が回転した基板素材に下することが好ましい。

【0016】また本発明は、前記選択成長で、基板素材上に塗布された粒子の塗布：ンチメートル当たり $1\times 10^9$ 個以上である。さらに好ましくは、塗布密度が $1$ 平方：ル当たり $1\times 10^9$ 個以上である。

【0017】また本発明は、前記選択成長で、用いる基板素材がシリコンであること

【0018】また本発明は、前記選択成長で、基板素材上に積層した犠牲層がフォ：あることが好ましい。

【0019】また本発明は、前記選択成長で、ダイヤモンド膜が気相合成法によって形成することが好ましい。

【0020】本発明方法の構成によれば、ダイヤモンド膜を選択的に形成する方法：素材上の一部の領域に平均粒径が $0.1$ を分散させた溶液を塗布する工程と、前：ダイヤモンド膜を成長させる工程とを含む：するため、以下のような作用を奏すること

【0021】基板素材上に塗布された平均：以下の粒子は、ダイヤモンド膜形成：成長核のサイトとなる。それ故に、塗：や塗布付着を人為的に制御してやること



(4)

特開平 9 -

5

5

素材上にダイヤモンド膜を選択的に形成する方法であって、一部の領域に犠牲層を積層した基板素材上に平均粒径が $0.1\ \mu\text{m}$ 以下の粒子を分散させた溶液を塗布する工程と、前記犠牲層を除去する工程と、前記基板素材上にダイヤモンド膜を成長させる工程とを含むことを特徴とするため、以下のような作用を奏することができる。

【0023】すなわち、上記のように基板素材上に平均粒径が $0.1\ \mu\text{m}$ 以下の粒子を塗布することで容易にダイヤモンド膜の成長が可能となるが、塗布領域を分離する方法として犠牲層を用いることにより、ダイヤモンド膜の成長領域の分離が容易になると共に、微細なパターン形成が容易となる。

【0024】また前記本発明方法の構成によれば、基板素材上にダイヤモンド膜を選択的に形成する方法であって、基板素材上に平均粒径が $0.1\ \mu\text{m}$ 以下の粒子を分散させた溶液を塗布する工程と、前記溶液が塗布された領域の一部を除去する工程と、前記基板素材上にダイヤモンド膜を成長させる工程とを含むことを特徴とするため、上記構成と同様にダイヤモンド膜の成長領域の分離が容易になると共に、微細なパターン形成が容易となる。

【0025】また本発明方法の構成において、塗布する溶液中に分散させた粒子がダイヤモンドからなるという好ましい例によれば、成長核となる粒子がダイヤモンド粒子であるため、良質なダイヤモンド膜を得ることが可能となる。

【0026】また本発明方法の構成において、塗布する溶液中に分散させた粒子の量が溶液1リットル当たり $0.01\ \text{g}$ 以上、 $100\ \text{g}$ 以下、さらに望ましくは溶液1リットル当たり $0.1\ \text{g}$ 以上、 $20\ \text{g}$ 以下であるという好ましい例によれば、塗布粒子を核として成長するダイヤモンドが短時間で膜状となるのに十分な量の粒子数を、容易に基板素材上に塗布することが可能となる。その際の最適な粒子量としては、用いる粒子の粒径にも依存し、粒径が $0.01\ \mu\text{m}$ の場合概ね $1\ \text{g}$ 程度、粒径が $0.04\ \mu\text{m}$ の場合、概ね $16\ \text{g}$ 程度である。

【0027】また本発明方法の構成において、塗布する溶液中に分散させた粒子の数が溶液1リットル当たり $1 \times 10^9$ 個以上、 $1 \times 10^{10}$ 個以下、さらに望ましくは溶液1リットル当たり $1 \times 10^9$ 個以上、 $1 \times 10^{10}$ 個以下であ

好ましい例によれば、大きな面積の基板に均一にかつ再現性良く溶液を塗布すること。

【0030】また本発明方法の構成において塗布された粒子の塗布密度が1平方センチメートル当たり $1 \times 10^9$ 個以上、さらに望ましくは1平方センチメートル当たり $1 \times 10^9$ 個以上であるという例によれば、成長初期において大きなダイヤモンドを得ることができるため、短時間で膜を得ることができる。

【0031】また本発明方法の構成において基板素材がシリコンであるという好ましい例によれば、プロセス構成が容易になると共に、シリコンとダイヤモンド層との融合化が可能となる。

【0032】また本発明方法の構成において塗布した犠牲層がフォトリソ resist 材料であるという好ましい例によれば、通常用いられているフォトリソ工程を用いてパターンニングができるプロセス構成となる。

【0033】また本発明構成において、気相合成法によって形成されるという例によれば、容易に良質なダイヤモンド膜を形成できる。

【0034】

【発明の実施の形態】以下、実施例を用いて具体的に説明する。

【0035】＜第1の実施の形態＞図1は、本発明に係る選択成長方法の一実施例の概略図で、

【0036】まず基板素材を準備する。この基板素材として用いる材料は特に限定はないが、シリコンが良く用いられる。ここでは2インチのシリコン基板1を用いた。

【0037】続いてこのシリコン基板1を、超音波洗浄装置で洗浄した後、シリコン基板1上の平均粒径が $0.01\ \mu\text{m}$ のダイヤモンド粒子を含む溶液を塗布した。(図1(b))本実施例の純水に2gのダイヤモンド粒子2、に2リットルのエタノールを加えた溶液。すなわち、粒子量として溶液1リットル当たり $1 \times 10^9$ 個以上、 $1 \times 10^{10}$ 個以下であ

(5)

特開平 9 -

7

8

の炭化水素ガス、アルコール、アセトン等の有機化合物及び一酸化炭素などの炭素源を水素で希釈したものを用い、その原料ガスを分解することによって行なわれるものである。その際、さらに原料ガスに適宜酸素や水等を添加することもできる。適用可能な気相合成法に関しても特に限定はされないが、本実施例においてはマイクロ波プラズマCVD法によってダイヤモンド膜の形成を行った。マイクロ波プラズマCVD法は原料ガスにマイクロ波を印加することによってプラズマ化し、ダイヤモンドの形成を行なう方法である。具体的な条件としては、原料ガスに水素で1～10 vol %程度に希釈された一酸化炭素ガスを用いた。反応温度及び圧力はそれぞれ800～900℃及び25～40 Torrである。

【0039】以上のような方法でシリコン基板上にダイヤモンド膜を形成した結果、溶液を塗布した部分にのみダイヤモンド膜が成長していることが確認された。また成長したダイヤモンドが膜状となる製膜時間も、従来の偏付け処理でダイヤモンドを形成した場合と比較して、半分程度に短縮されることがわかった。このことはダイヤモンドの核発生密度が非常に大きいことに起因するものと考えられる。そこで本実施例におけるダイヤモンドの成長初期における核発生密度を調べた結果、1平方センチメートル当たり約 $1 \times 10^3$ 個と従来の基板前処理方法よりも1桁程度大きいことが確認された。すなわち、従来よりも効率的に良質なダイヤモンド膜が選択成長できることが確認された。

【0040】また他の形成条件でダイヤモンド膜を成長した場合や塗布するダイヤモンド粒子の粒径や量を変えて溶液を調合した場合、さらには粒子をシリコンカーバイドに変えた場合などにおいても、同様の結果が得られた。

【0041】＜第2の実施の形態＞図2は本発明方法に係る選択成長法の他の一実施例の概略図である。

【0042】まず基板素材を準備する。(図2(a))本構成においても基板素材材料は特に限定されないが、本実施例では2インチのシリコン基板4を用いた。

【0043】次にこのシリコン基板4を通常の洗浄工程で洗浄した後、厚さ約2  $\mu\text{m}$ のフォトレジスト材5を塗布した。(図2(b))塗布方法については限定されるものではないが、本実施例では回転させたシリコン基

材5が積層されたシリコン基板4上に、 $0.1 \mu\text{m}$ のダイヤモンド粒子6を分散させた。(図2(d))用いた溶液は、第1の実施例と同様のスピンコートの手法を用い、シリコン基板4は赤外線ランプ光の照射にした。

【0046】その後、ダイヤモンド粒子シリコン基板4をレジスト除去用の溶剤に浸し、フォトレジスト材5を除去した。レジスト除去用の溶剤としては、用いるの材質等に依存するが、一般的にアセト剤を用いることができる。

【0047】さらにフォトレジスト材5シリコン基板4上にマイクロ波プラズマCVDでダイヤモンド膜7を形成した。(図2(e))形成条件は、第1の実施例と同様である。【0048】以上のような方法でシリコン基板上にダイヤモンド膜を形成した結果、溶液を塗布した領域にのみダイヤモンド膜が成長していることが確認された。またフォトレジスト除去の際にレジスト除去用の溶剤に浸し、形成されたダイヤモンド膜のフォトレジスト除去前にダイヤモンド粒子6が塗布した領域のパターンと同一であり、また成長速度も第1の実施例と同様であった。一端ダイヤモンド粒子が基板素材上に塗布された後、ファンデルワールス力などの方で安定に付着していることを示している。

【0049】本実施例においては、粒子6を別するマスク材としてフォトレジストを用いた場合でも良く例えばアモルファスシリコンを堆積した後パターニングして、マスク材様の結果が得られた。

【0050】また他の形成条件でダイヤモンド膜を成長した場合や塗布するダイヤモンド粒子の粒径や量を変えて溶液を調合した場合、さらには粒子をシリコンカーバイドに変えた場合などにおいても、同様の結果が得られた。

【0051】＜第3の実施の形態＞通常の

(6)

特開平 9 -

9

10

用いた。

【0053】続いてこのシリコン基板8を通常の洗浄工程で洗浄した後、シリコン基板8を石英製の円筒容器に設置し、ウェットな酸素雰囲気中で加熱する熱酸化を行なった。熱酸化条件は1000℃、2時間である。その結果、シリコン基板8の表層約1μmの領域に二酸化シリコン層9が形成された(図3(b))。

【0054】次に厚さ約2μmのフォトレジスト材10をスピンコートで塗布した後、通常のフォトリソグラフィの工程でフォトレジスト材10に所望のパターンを形成した。(図3(c))形成パターンは、第2の実施例と同様である。

【0055】さらに、そのフォトレジスト材10をマスクとして、シリコン基板表層の二酸化シリコン層9をエッチング除去した。(図3(d))二酸化シリコン層9のエッチングは、フッ硝酸系のエッチング液を用いたウェットエッチングにより行なった。その結果、第2の実施例と同様、二酸化シリコン層9が除去された部分に直径が5μmの丸いドットの窓が形成された。

【0056】そしてパターンニングされたフォトレジスト材10及び二酸化シリコン層9が積層されたシリコン基板8上に、平均粒径が0.01μmのダイヤモンド粒子11を分散させた溶液を塗布した。(図3(e))用いた溶液は、第1の実施例と同様である。溶液の塗布は、フォトレジスト材を塗布したのと同様のスピンコートの手法を用いた。塗布後、シリコン基板8は赤外線ランプ光の照射によって乾燥された。

【0057】その後、ダイヤモンド粒子11が塗布されたシリコン基板8をレジスト除去用の溶剤に10分以上浸し、フォトレジスト材10を除去した。(図3(f))さらにフォトレジスト材10が除去されたシリコン基板8上にマイクロ波プラズマCVD法によってダイヤモンド膜12を形成した。(図2(g))ダイヤモンド膜の合成条件は、第1の実施例と同じである。

【0058】以上のような方法でシリコン基板上にダイヤモンド膜を形成した結果、溶液を塗布した部分すなわち直径が5μmのドット領域にのみダイヤモンド膜が成長していることが確認された。そして第2の実施例と比較した結果、その選択成長性の向上が確認された。

【0059】本実施例においては、ダイヤモンドが成長

【0062】まず基板素材を準備する。本構成においても基板素材材料は特に限定されず、ほん実施例では2インチのシリコン基板を用いた。

【0063】次にシリコン基板13を通常の洗浄工程で洗浄した後、シリコン基板13上に平均1μmのダイヤモンド粒子14を分散させた。(図4(b))用いた溶液は、第2の実施例と同様である。溶液の塗布は、第2の実施例のスピンコートの手法を用いた。塗布後、シリコン基板13は赤外線ランプ光の照射によって乾燥された。

【0064】続いて厚さ約2μmのフォトレジスト材15をスピンコートで塗布した(図4(c))

【0065】そして、通常のフォトリソグラフィの工程でフォトレジスト材15に所望のパターンを形成した。(図4(d))本実施例においては、シリコン基板13上に直径が5μmの丸いドットを20μm間隔で100×100個からなるドットを塗布した。フォトレジスト材15で形成して、他の部分は除去した。

【0066】さらにパターンニングされたフォトレジスト材15をマスクとして、シリコン基板13上の二酸化シリコン層9をエッチングした。(図4(e))エッチングには、特に限定はされないが、本実施例では、フロンガスを用いた反応性イオンエッチング(RIE)により未マスク領域のシリコン基板13をエッチング除去した。

【0067】その後、フォトレジスト材15を除去用の溶剤で除去した(図4(f))

【0068】さらにフォトレジスト材15が除去されたシリコン基板13上にマイクロ波プラズマCVD法によってダイヤモンド膜16を形成した。(図4(g))ダイヤモンド膜の合成条件は、第1の実施例と同じである。

【0069】以上のような方法でシリコン基板上にダイヤモンド膜を形成した結果、溶液を塗布した部分すなわち直径が5μmのドット領域にのみダイヤモンド膜が成長していることが確認された。またフォトレジスト材を除去する際にレジスト除去用の溶剤に浸し、形成されたダイヤモンド膜の表面を洗浄し、形成されたダイヤモンド膜の表面にフォトレジスト除去前にダイヤモンド粒子

(7)

特開平 9 -

11

12

て溶液を調合した場合、さらには粒子をシリコンカーバイドに変えた場合などにおいても、同様の結果が得られた。

【0072】＜比較例＞上記に記載した実施例との比較のために、溶液中に0.1  $\mu\text{m}$  よりも大きなダイヤモンド粒子を混合して同様の実験を行なった。その結果、ダイヤモンド成長の初期過程における核発生密度は、上記実施例と比較して1桁以上低く、その結果膜状となるのに2倍以上の製膜時間が必要であった。また基板表面内の膜厚分布にムラがあり、均一性に乏しかった。さらには粒子塗布部と未塗布部との選択成長性も著しく低下することが確認された。

【0073】

【発明の効果】以上のように、本発明方法に係る選択成長方法の構成によれば、基板素材上にダイヤモンド膜を選択的に形成する方法であって、基板素材上の一部の領域に平均粒径が0.1  $\mu\text{m}$  以下の粒子を分散させた溶液を塗布する工程と、前記基板素材上にダイヤモンド膜を成長させる工程とを含むことを特徴とするため、成長するダイヤモンド膜の均一性や再現性が格段向上すると共に、ダイヤモンド膜成長と同時に、所望のダイヤモンド膜パターンを得ることが可能となる。

【0074】また本発明方法に係る選択成長方法の構成によれば、基板素材上にダイヤモンド膜を選択的に形成する方法であって、一部の領域に犠牲層を積層した基板素材上に平均粒径が0.1  $\mu\text{m}$  以下の粒子を分散させた溶液を塗布する工程と、前記犠牲層を除去する工程と、前記基板素材上にダイヤモンド膜を成長させる工程とを含むことを特徴とするため、効率的にダイヤモンド膜が成長すると共に、ダイヤモンド膜の成長領域の分離が容易になるので、微細なパターン形成が容易となる。

【0075】また本発明方法に係る選択成長方法の構成によれば、基板素材上にダイヤモンド膜を選択的に形成する方法であって、基板素材上に平均粒径が0.1  $\mu\text{m}$  以下の粒子を分散させた溶液を塗布する工程と、前記溶液が塗布された領域の一部を除去する工程と、前記基板素材上にダイヤモンド膜を成長させる工程とを含むことを特徴とするため、上記構成と同様にダイヤモンド膜の成長領域の分離が容易になるので、微細なパターン形成が容易となる。

数を溶液1リットル当たり  $1 \times 10^9$  個以下、さらに望ましくは溶液1リットル1個以上、  $1 \times 10^9$  個以下とすることにより、同様に、短時間でダイヤモンドが膜状との粒子数を容易に基板素材上に塗布する。

【0079】さらに塗布する溶液を水あるとすることにより、溶液の扱いが容易

【0080】さらに溶液の塗布方法を回への溶液滴下とすることにより、大きなに対して均一にかつ再現性良く溶液を可能となる。

【0081】さらに基板素材上に塗布さ密度を1平方センチメートル当たり  $1 \times$  らに望ましくは1センチメートル当たりとすることにより、短時間で膜状のダイヤモンドができる。

【0082】さらに用いる基板素材をシとにより、プロセス構成が容易になるとを用いた素子とダイヤモンド層との融合る。

【0083】さらに基板素材上に積層しトレジスト材とすることにより、通常用フォトリソグラフィ工程を用いてパターンで、簡便なプロセス構成となる。

【0084】さらにダイヤモンド膜を気て形成することにより、容易に良質なダイヤモンド形成することができる。

【図面の簡単な説明】

【図1】本発明方法に係る選択成長方法す概略図

【図2】本発明方法に係る選択成長方法を示す概略図

【図3】本発明方法に係る選択成長方法を示す概略図

【図4】本発明方法に係る選択成長方法を示す概略図

【符号の説明】

1 シリコン基板

2 ダイヤモンド粒子

(8)

特開平 9 -

14

13

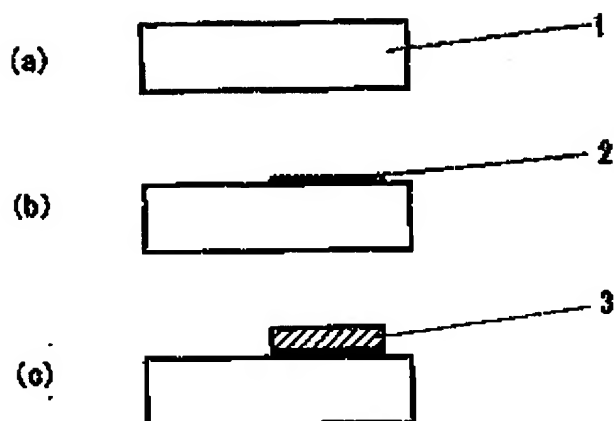
13 シリコン基板

14 ダイヤモンド粒子

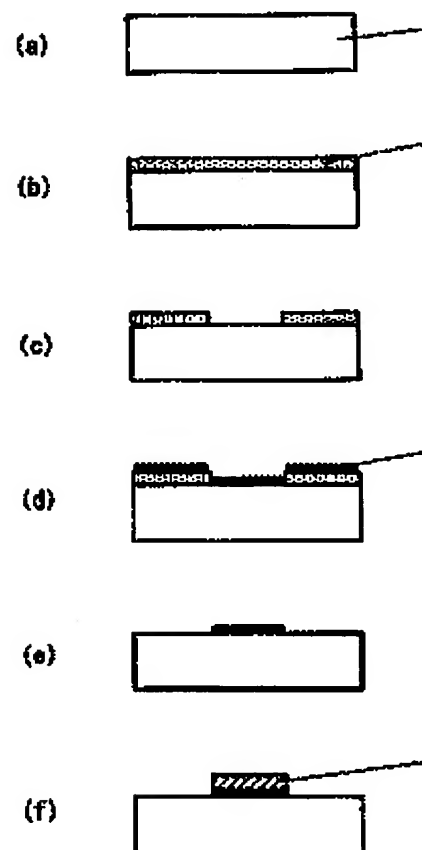
\* 15 フォトレジスト材

\* 16 ダイヤモンド膜

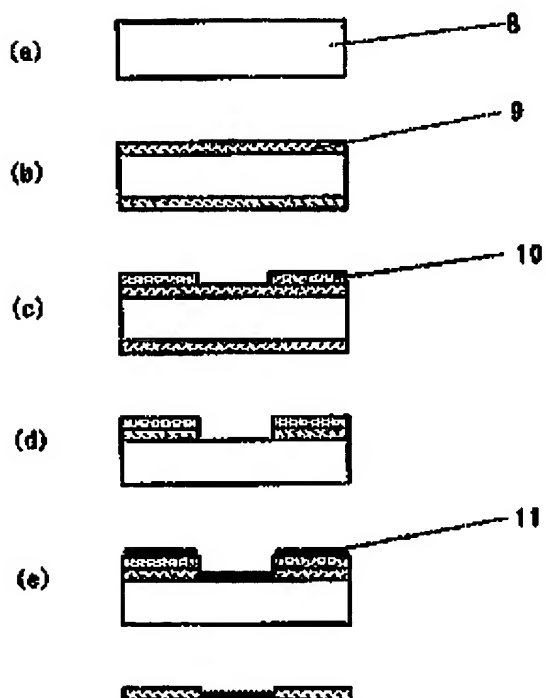
【図 1】



【図 2】



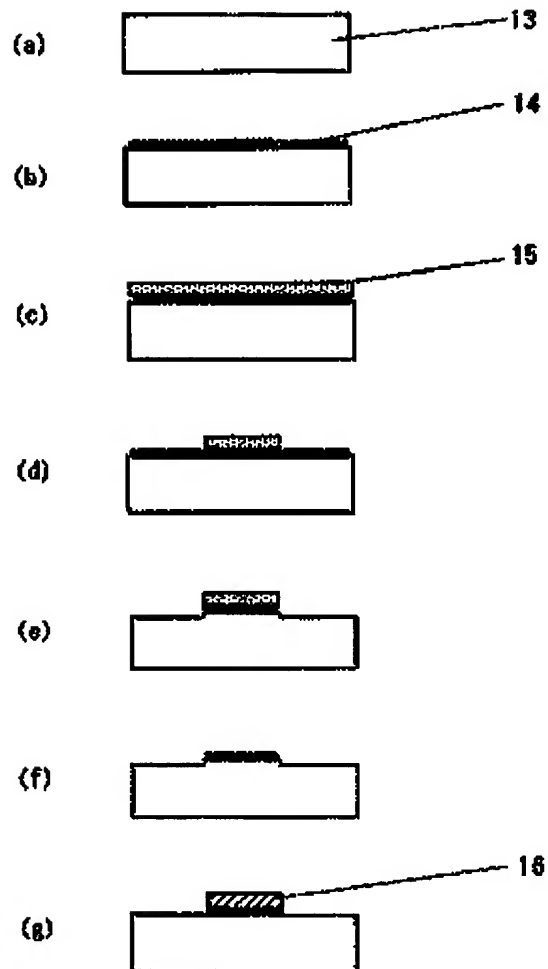
【図 3】



(9)

特開平 9 -

【図 4】



フロントページの続き

(72)発明者 牧田 寛  
兵庫県川西市向陽台 2 - 1 - 59

(72)発明者 北島 真  
大阪府門真市大字門真1006  
産業株式会社内

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record.**

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☒ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☒ **GRAY SCALE DOCUMENTS**
- ☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**